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(54) **Polyurethane resins in water dilutable basecoats having low flash and quick-drying characteristics.**

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Description

Multi-layer systems have been utilized to coat automobiles for a number of years, but the early development of these systems necessarily employed organic solvents. As environmental regulations became more stringent, and the cost of organic solvents rose, organic-borne basecoat systems became less desirable. The recent research emphasis in the area of multi-layer systems, especially basecoat systems has focused on the development of water-borne systems for multi-layer coatings.

The shift from organic solvents to water for dispersing and applying resins in multi-layer systems solved many of the environmental and cost problems associated with the use of organic solvents. Water-borne systems, however, have resulted in other problems.

The application of a multi-layer coating to an automobile body, for example, would be greatly facilitated by a system that provides for quick-drying of solvent during and after the application of a coating. These quick-drying characteristics enhance a broad application window and allow minimal control of relative humidity and temperature in the spray zone, resulting in lower energy costs. By facilitating drying, the time between coatings would be diminished, resulting in greater manufacturing efficiencies and lower energy costs. In addition, there would be no need for a cool-down zone after drying which would further the manufacturing efficiencies. Low boiling organic solvents were originally used in multi-layer coatings to take advantage of their quick-drying features. With the introduction of aqueous based multi-layer systems, the drying of water from a given resin coating after application became a problem. It was desired to provide waterborne basecoat compositions with low-flash and quick-drying characteristics and having favorable coating and cosmetic characteristics.

EP-A-89 497 and EP-A-228 003 disclose the use of an anionic polyurethane resin for producing waterborne basecoat compositions for multi-layer coatings wherein said polyurethane resin comprises the reaction product of

- (a) a polyester polyol
- (b) a multi-functional compound having at least one active hydrogen functionality and at least one carboxylic acid functionality, said carboxylic acid groups being at least partially neutralized with base to form salt groups
- (c) a compound having at least two active hydrogen groups but having no carboxylic acid groups and
- (d) a polyisocyanate.

EP-A-89 497 and EP-A-228 003 also disclose a method of coating a substrate with a multi-layer coating comprising

- (A) applying to the substrate a first layer of waterborne basecoat composition comprising
 - (i) an anionic polyurethane resin comprising the reaction product of
 - (a) a polyester polyol
 - (b) a multi-functional compound having at least one active hydrogen functionality and at least one carboxylic acid functionality, said carboxylic acid groups being at least partially neutralized with base to form salt groups
 - (c) a compound having at least two active hydrogen groups but having no carboxylic acid groups and
 - (d) a polyisocyanate
 - (ii) a pigment or a mixture of pigments
- (B) flash drying said first layer
- (C) applying at least one layer of a clear topcoat onto said basecoat and
- (D) curing said basecoat and topcoat to a hard, durable film.

It is an object of this invention to improve the method disclosed in EP-A-89 497 and EP-A-228 003.

In particular, this invention relates to the discovery that incorporating a long-chain carboxylic acid of at least 50% by weight of the carboxylic acid component used to make polyester polyols which are further incorporated into polyurethane resins provides basecoat compositions exhibiting low temperature flash characteristics. These low temperature flash characteristics are exhibited even where the basecoats are deposited at 50-90% relative humidity.

Thus according to the present invention there is provided the use of an anionic polyurethane resin for producing waterborne basecoat compositions for multi-layer coatings wherein said polyurethane resin has an acid number of at least about 10 and comprises the reaction product of

- (a) a polyester polyol
- (b) a multi-functional compound having at least one active hydrogen functionality and at least one carboxylic acid functionality.

(c) optionally a compound having at least two active hydrogen groups but having no carboxylic acid groups

(d) a polyisocyanate and

(e) a base for purposes of at least partially neutralizing the carboxylic acid groups

- 5 characterized in that said polyester polyol (a) is synthesized from a carboxylic acid component and an excess of a polyol component wherein said carboxylic acid component comprises at least 50 % by weight of at least one long-chain carboxylic acid having between 18 and 60 carbon atoms.

According to the present invention there is also provided a method of coating a substrate with a multilayer coating comprising

- 10 (A) applying to the substrate a first layer of waterborne basecoat composition comprising

(i) an anionic polyurethane resin as described above

(ii) a pigment or a mixture of pigments and

(iii) a rheology control agent

(B) flash drying said first layer

- 15 (C) applying at least one layer of a clear topcoat onto said basecoat and

(D) curing said basecoat and topcoat to a hard, durable film

characterized in that said polyester polyol (a) is synthesized from a carboxylic acid component and an excess of a polyol component wherein said carboxylic acid component comprises at least 50 % by weight of at least one long-chain carboxylic acid having between 18 and 60 carbon atoms.

- 20 The waterborne basecoat compositions produced by using the anionic polyurethane resin according to the present invention exhibit low-flash and quick-drying characteristics and furthermore superior coating characteristics such as very favorable arrangement and fixation of the metallic pigments in the paint film. The multi-layer coatings produced by using these basecoat compositions exhibit good metallic effects. When non-metallic pigments are used, the coatings exhibit excellent decorative effect.

- 25 The anionic polyurethane resin described above can be formulated as a water-dispersed basecoat resin along with a grind resin, a cross-linking agent, thixotropic or rheology control agents, thickeners, pigments, aluminum and/or mica particles, basifying agents, water, fillers, surfactants, stabilizers, plasticizers, wetting agents, dispersing agents, adhesion promoters, defoamers, catalysts, and additional polymers, for example a branch-chain polyester among other ingredients.

- 30 After formulation, the basecoat composition can be sprayed or electrostatically deposited onto the automobile body, preferably, in one or two coats. Generally, two even coats of basecoat are applied with a one minute flash between coats. After deposition of the basecoat, before application of a high solids content clear coat, it is generally preferred to flash about 90% of the water from the basecoat for optimum appearance and to eliminate water boil of the clearcoat.

- 35 The polyester polyol (a) is formed from an alcohol component having at least about 2 hydroxy groups per molecule (polyol) and a carboxylic acid component. The carboxylic acid component is comprised of at least 50% by weight of at least one long chain carboxylic acid having between 18 and 60 carbon atoms in the chain. This long-chain carboxylic acid component is an alkyl, alkylene, aralkyl, aralkylene, or compound of similar hydrophobicity having 18 and 60 carbons in the chain. The polyester polyol chain may be
40 branched, but it is preferred that chain-branching be kept to a minimum. It is recognized that low flash and quick-drying characteristics of the basecoat compositions of this invention are the result of having a high percentage of highly hydrophobic groups in the polyester polyol resin. C18 to C60 carboxylic acid present a range of compounds having suitable hydrophobicity. Most preferably, this long chain carboxylic acid is a dicarboxylic acid and most preferably is a C₃₆ dicarboxylic acid known as a dimer acid. The remaining
45 carboxylic acid component may be comprised of a short-chain monocarboxylic or dicarboxylic acid component, preferably a dicarboxylic acid. When monocarboxylic acid compounds are used, these function as polyester chain terminators. Thus, where high molecular weight polyesters are desired, the amount of monocarboxylic acid is kept to a minimum. The short-chain dicarboxylic acid may be preferably short-chain alkyl or alkylene dicarboxylic acid, for example, azelaic acid, adipic acid, or an equivalent aliphatic
50 dicarboxylic acid or an aromatic dicarboxylic acid. Most preferably, the aromatic dicarboxylic acid is isophthalic acid. It must be stressed that while a number of short-chain carboxylic acid compounds may be used, the ultimate goal is to maintain the hydrophobic, quick-flash characteristics of the polyester polyol resin.

- 55 The composition of the carboxylic acid component and polyol component employed to synthesize the polyester polyol resins is such as to provide an excess of the polyol over and above the total number of equivalents of acid present in the mixture. In other words, the reactants should be selected, and the stoichiometric proportions of the respective acid and polyol components be adjusted to give hydroxy-terminated, polyester molecules each theoretically having a hydroxyl functionality of 2 or more.

As stated above, the acid mixture employed in forming the polyester polyol intermediate most preferably contains a C₃₆ dicarboxylic acid product known as dimer acid. Processes for forming this acid are well known and form the subject of numerous U.S. patents including Nos. 2,482,761, 2,793,220, 2,793,221 and 2,995,121 or alternatively dimer fatty acid can be purchased from a chemical supply house (Empol 1010™, available from Emery Chemical Co.)

C₃₆ dimer fatty acid fraction consists essentially of dimer (C₃₆ dicarboxylic acids) together with amounts up to about 20-22% of C₅₄ trimer. However, those of skill in the art refer to this dimer-trimer mixture as "dimer", and this practice is followed herein. The preferred grade contains 97% dimer and 3% trimer. These polymerization reaction products can be used in the form in which they are recovered from the polymerization unit, or they can be given a partial or complete hydrogenation treatment to reduce unsaturation before being reacted with the polyol compound to form the polyester polyol (a).

Preferably, the long chain fatty acid comprises between about 50 and 80% by weight of the acid component of the polyester polyol.

Generally, the higher the percentage of long chain carboxylic acid, the better the quick-drying or flash off characteristics of the final polyurethane resin. However, the advantageous flash-off characteristics must be balanced with the effect that the change in the carboxylic acid component has on the metallic effects, durability and other characteristics of the resin, including, in the case of grind resin, the ability to accomodate pigment.

The shorter chain carboxylic acid component is comprised of a mono-, di- or higher functionality carboxylic acid or a mixture of these carboxylic acids having carbon chains of 12 or fewer carbon units. Monocarboxylic acids function to terminate a polyester chain and are chosen for that purpose. It is preferable that the short chain carboxylic acid component be a dicarboxylic acid. Such preferred dicarboxylic acid compounds include, for example, adipic, azeleic, and other aliphatic dicarboxylic acids. Aromatic dicarboxylic acids may also be preferred. An especially preferred aromatic dicarboxylic acid is isophthalic acid. Alkylene and aralkylene carboxylic acids can also be used. Where branch chains in the polyester polyol are desired, a carboxylic acid containing three or more carboxylic acid groups, for example citric acid, is used. A preferred acid of this type is trimellitic anhydride.

The polyester resin in most cases is comprised of one or more polyols, preferably a diol. Up to about 25 percent by weight of the polyol component may be a polyol having three or more hydroxy groups per molecule. Where polyols having three or more hydroxy groups are chosen, the result is a branched polyester polyol.

While it is not always desirable to have a triol or higher multi-functional alcohol present because of the tendency to form a branched chain polyester polyol, some branching may be desirable. The polyester polyol resin should not be highly branched, however. There may also be present a small amount of monoalcohol, in the polyol component, particularly if larger proportions of higher functional alcohols are used. These monoalcohols serve as chain terminators. In certain instances, for example, where certain high molecular weight polyols are used, the polyols can be largely or even entirely made up of compounds of functionality greater than two.

The diols which are usually employed in making the polyester polyol resins include alkylene glycols, such as ethylene glycol, propylene glycol, butylene glycol, and neopentyl glycol, 1,6 hexanediol and other glycols such as hydrogenated bisphenol A, cyclohexane dimethanol, caprolactone diol (i.e., the reaction product of caprolactone and ethylene glycol), hydroxyalkylated bisphenols. However, other diols of various types and, as indicated, polyols of higher functionality may also be utilized. Such higher functional alcohols can include, for example, trimethylolpropane, trimethylethane, pentaerythritol as well as higher molecular weight polyols.

The low molecular weight diols which are preferred in the instant invention are known in the art. They have hydroxy values of 200 or above, usually within the range of 2000 to 200. Such materials include aliphatic diols, particularly alkylene polyols containing from 2 to 18 carbon atoms. Examples include ethylene glycol, 1,4-butanediol, cycloaliphatic diols such as 1,2 cyclohexanediol and cyclohexane dimethanol. An especially preferred diol is 1,6 hexanediol.

The resulting polyester polyol resin is preferably produced with dimer fatty acid as the long chain carboxylic acid, isophthalic acid as the minor short-chain carboxylic acid component and an excess of 1,6 hexane diol so that the resulting polyester polyol ranges in size between 200 and 2000 grams per equivalent of hydroxyl. Preferably, the polyester resin has a range between 700 and 800 grams per equivalent of hydroxyl and most preferably, has about 750 grams per equivalent of hydroxyl.

To produce the polyurethane resins which are useful in basecoat compositions of the present invention, the above described polyester polyol (a) is reacted with

(b) a multi-functional compound having at least one active hydrogen functionality and at least one carboxylic acid functionality

(c) optionally a compound having at least two active hydrogen groups but having no carboxylic acid groups

5 (d) a polyisocyanate and

(e) a base for purposes of at least partially neutralizing the carboxylic acid group.

The polyester polyol, polyisocyanate and multi-functional compound may be reacted in the same pot, or may be reacted sequentially, depending upon the desired results. Sequential reaction produces resins which are more ordered in structure. Both the polyester polyol and multi-functional compound may serve as
10 chain extenders to build up the polyurethane backbone through reaction of hydroxyl groups with isocyanate groups. However, to function as a chain extender, the multi-functional compound must have at least two active hydrogen groups. Where the multi-functional compound has only one active hydrogen group, the result is chain termination. Additional chain extenders having at least two active hydrogen groups but no carboxylic acid groups may be added to increase the chain length or to change the chemical characteristics
15 of the polyurethane resin. Preferably, an excess of polyisocyanate is used so that an intermediate polyurethane resin can be produced having free isocyanate groups at the terminal ends. The free isocyanate groups may then be preferably capped with an excess of an alcohol having a hydroxy functionality of at least one and preferably two or more e.g. trimethylol propane or diethanolamine.

The organic polyisocyanate (d) which is reacted with the polyhydric material as described is essentially
20 any polyisocyanate and is preferably a diisocyanate, e.g., hydrocarbon diisocyanates or substituted hydrocarbon diisocyanates. Many such organic diisocyanates are known in the art, including p-phenylene diisocyanate, biphenyl 4,4'-diisocyanate, toluene diisocyanate, 3,3'-dimethyl-4,4' biphenylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethylhexane-1,6 diisocyanate, methylene bis (phenyl isocyanate), 1,5 naphthalene diisocyanate, bis (isocyanatoethyl fumarate), isophorone
25 diisocyanate (IPDI) and methylene-bis- (4 cyclohexylisocyanate). There can also be employed isocyanate-terminated adducts of polyols, such as ethylene glycol, or 1,4-butylene glycol trimethylolpropane, etc. These are formed by reacting more than one mol. of a diisocyanate, such as those mentioned, with one mol. of a polyol to form a longer chain diisocyanate. Alternatively, the polyol can be added along with the diisocyanate.

30 While diisocyanates are preferred, other multi-functional isocyanates may be utilized. Examples are 1,2,4-benzene triisocyanate and polymethylene polyphenyl isocyanate.

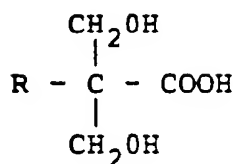
It is preferred to employ an aliphatic diisocyanate, since it has been found that these provide better color stability in the finished coating. Examples include 1,6-hexamethylene diisocyanate, 1,4-butylene diisocyanate, methylene bis (4-cyclohexyl isocyanate) and isophorone diisocyanate. Mixtures of
35 diisocyanates can also be employed.

The proportions of the diisocyanate, polyester polyol, and multi-functional compound preferably are chosen so as to provide an isocyanate terminated intermediate polyurethane resin. This can be accomplished by utilizing a stoichiometric excess of polyisocyanate, i.e., more than one isocyanate group per nucleophilic moiety (reactive with isocyanate) in the other components.

40 For purposes of promoting water-solubility it is important to build acid groups into the polyurethane. For example, the presence of acid groups is capable of rendering the composition water-dilutable.

The acids (component (b)) that are employed to provide free acid groups in the polyurethane resins of this invention are readily available. They contain at least one active hydrogen group and at least one carboxylic acid functionality. The active hydrogen group may be a thiol, a hydroxyl or an amine, with
45 primary amines being considered to have one active hydrogen group. Examples of such compounds include hydroxyl carboxylic acids, amino acids, thiol acids, aminothiol acids, alkanolamino acids, and hydroxythiol acids.

Compounds containing at least 2 hydroxyl groups and at least one carboxylic acid are preferred. They can be prepared from an aldehyde that contains at least two hydrogens in the alpha position. Such
50 aldehydes are reacted in the presence of a base catalyst with two equivalents of formaldehyde to form a 2,2-hydroxymethyl aldehyde. The aldehyde is then gently oxidized to the acid by known procedures. The acids that are employed in the invention can be represented in simplification by Formula I:



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wherein R represents hydroxymethyl, hydrogen, or alkyl of up to 20 carbon atoms and preferably up to 8 carbon atoms.

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Specific illustrative examples of such acids that are employed in the invention include 2,2-di(hydroxymethyl) acetic acid, 2,2,2-tri(hydroxymethyl) acetic acid, 2,2-di(hydroxymethyl) propionic acid, 2,2-di(hydroxymethyl) butyric acid, and 2,2-di(hydroxymethyl) pentanoic acid. The preferred acid is 2,2-di(hydroxymethyl) propionic acid.

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Longer-chain polyurethane resins can be obtained by chain extending the polyurethane chain with a compound or mixture of compounds containing at least two active hydrogen groups but having no carboxylic acid group (component (c)), for example diols, dithiols, diamines, or compounds having a mixture of hydroxyl, thiol, and amine groups, for example, alkanolamines, aminoalkyl mercaptans, and hydroxyalkyl mercaptans, among others. For purposes of this aspect of the invention both primary and secondary amine groups are considered as having one active hydrogen. Alkanolamines, for example, ethanolamine or diethanolamine, are preferably used as chain extenders, and most preferably, a diol is used. Examples of preferred diols which are used as polyurethane chain extenders include 1,6 hexane diol, cyclohexanedimethylol, and 1,4-butanediol. A particularly preferred diol is neopentylglycol. Of course, the same diols used to synthesize the polyester component of the polyurethane resins can be utilized here as well. While polyhydroxy compounds containing at least three hydroxyl groups may be used as chain extenders, the use of these compounds produces branched polyurethane resins. For purposes of the present invention, it is preferred to minimize the amount of branching in the polyurethane resin. Therefore, if polyhydroxy compounds are used, they are preferably limited to a very minor component of the polyurethane producing mixture. These higher functional polyhydroxy compounds include, for example, trimethylolpropane, trimethylolethane, and pentaerythritol.

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The polyurethane resin may be chain extended in any manner using these compounds having at least two active hydrogen groups. Thus, these compounds may be added to the mixture of polyisocyanate, polyester polyol and multi-functional compound, or alternatively, may react at an intermediate stage, to link two free isocyanate groups that are present at the terminal ends of an intermediate polyurethane resin.

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It is generally preferred that an intermediate polyurethane resin produced by reacting the polyester polyol resin and the mixture of polyisocyanate, multifunctional compound containing at least 2 hydroxyl groups and one carboxylic acid group, and chain extender be terminated with free isocyanate groups. To accomplish this, an excess of the polyisocyanate component is used. Of course, the molar ratio of the other components will be adjusted according to the desired characteristics of the intermediate and final polyurethane resins. The polyester polyol component comprises no more than about 80% by weight of the reaction mixture and it is preferred that the polyester component comprises from 20% to 70% by weight of reactants in the mixture.

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In one especially desirable embodiment of the invention, a multi-functional alcohol is used to terminate the reaction (cap the free isocyanate groups) at the desired stage (determined by the viscosity and isocyanate groups present), thereby also contributing residual hydroxyl groups. Particularly desirable for such purposes are aminoalcohols, such as ethanolamine, diethanolamine and the like, since the amino groups preferentially react with the isocyanate groups present. Multi-functional alcohols, such as ethylene glycol, trimethylolpropane and hydroxyl-terminated polyesters, can also be employed in this manner.

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While the ratios of the components of the polyester polyol the multi-functional isocyanate and the terminating agent can be varied, it will be noted by those skilled in the art that the amounts should be chosen so as to avoid gellation and to produce an ungelled, urethane reaction product containing hydroxyl groups. The hydroxyl value of the urethane reaction product should be at least 5 and preferably about 20 to about 200.

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The amount of polyisocyanate used in the mixture is preferably between about 20% and 30% by weight of the reactants in the mixture, but will vary depending upon the polyester polyol used, the acid number of the final polyurethane resin, and the desired molecular weight of the final polyurethane resin. The amount of polyisocyanate will also vary depending upon whether it is desired to have the intermediate polyurethane terminated with free isocyanate groups or with hydroxyl groups. Thus, where it is preferred to terminate the

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intermediate polyurethane resin with free isocyanates for capping with trimethylolpropane or diethanolamine, an excess of polyisocyanate may be used. Where the intermediate polyurethane resin is to be terminated by hydroxyl groups, a stoichiometric deficiency of polyisocyanate may be used.

The amount of multi-functional component having at least one active hydrogen group and at least one carboxylic acid group also may vary depending upon the desired acid number of the final polyurethane resin. The final polyurethane resin has an acid number of at least about 10, and the amount of this multi-functional component comprises between 1% and 25% by weight of the reactants of polyurethane producing reaction mixture (polyisocyanate, polyester polyol, multifunctional compound, and optionally other chain extenders, for example compounds having two active hydrogens but no carboxylic groups). It is preferable that the acid number be higher, because as the acid number increases, the water-dispersibility of the polyurethane resin potentially increases. The practical upper limit of acid number is that which negatively effects the low flash or quick-drying characteristics and physical properties of the final resin. Of course, the upper limit of the acid number will vary depending upon the chemical composition of the final polyurethane resin, but an acid number with an upper limit of about 100 is, in general, the practical limit of polyurethane resins of the present invention.

The amount of chain extender, when used producing the polyurethane resin, varies between 2% and 25% by weight of the reactants. The amount used will depend upon the amount of chain extension desired and the desired size of a polyurethane molecule.

After the polyurethane resin is synthesized, the free carboxylic acid groups are neutralized with base to form salt groups. Preferably, the base is an amino containing compound. Tertiary amines are generally preferred over primary and secondary amines because of the tendency of the primary and secondary amines to react with aminoplast cross-linking agents. Preferred tertiary amines include tri-alkylamines, for example, trimethyl and triethylamine. Also preferred is triethanolamine. Particularly preferred is dimethylethanolamine.

The anionic polyurethane resins used according to the present invention are advantageously storage stable and are, of course, water dispersible. The water dispersibility of the resins is controlled by the amount of free carboxylic acid contained in the final resin particles, and the number of salt groups formed from those free acid groups.

The polyurethane resins of the present invention are formulated, along with other components, into water dispersible basecoat compositions which are sprayed or electrostatically deposited onto metal or plastic substrates, for example, automobile bodies. In general, a polyurethane resin formulated as described herein, is mixed with an aminoplast resin, pigments, a grind resin, water, a portion of an organic solvent, aluminum and/or mica particles and a rheology control agent. Other agents may be included, for example, various fillers, surfactants, plasticizers, stabilizers, wetting agents, dispersing agents, defoamers, adhesion promoters and catalysts in minor amounts. In one preferred embodiment a branched-chain polyester component is also added to the basecoat composition.

As indicated, an aqueous dispersion of the anionic polyurethane resin is utilized as the principal or major vehicle resin. In general, the principal or major vehicle resin comprises between about 20 and 80% by weight of the total solids present in the basecoat composition. The preferred polyurethane resin is a resin produced from a polyester synthesized from dimer fatty acid, isophthalic acid, and 1,6 hexanediol. The resulting polyester is then reacted with a diisocyanate of isophorone, dimethylol propionic acid and a diol, for example, neopentyl glycol. The resulting polyurethane intermediate having free isocyanate groups is then reacted with trimethylolpropane to cap these groups.

The polyurethane reaction product as described above preferably is mixed with an aminoplast resin. Aminoplast resins are aldehyde condensation products of melamine, urea, and similar compounds. Products obtained from the reaction of formaldehyde with melamine, urea or benzoguanamine are most common and are preferred herein. However, condensation products of other amines and amides can also be employed, for example, aldehyde condensates of triazines, diazines, triazoles, guanidines, guanamines and alkyl and aryl substituted derivatives of such compounds, including alkyl and aryl substituted ureas and alkyl and aryl substituted melamines. Some examples of such compounds are N,N'-dimethylurea, benzourea, dicyan-diamide, formoguanamine acetoguanamine, ammeline, 2-chloro-4,6-diamino- 1,3,5-triazine, 6-methyl-2,4-diamino,1,3,5-triazine, 3-5- diamino-triazine, triaminopyrimidine, 2-mercapto-4,6- diaminopyrimidine and 2,4,6-triethyl triamino-1,3,5-triazine.

While the aldehyde employed is most often formaldehyde, other similar condensation products can be made from other aldehydes, for example, acetaldehyde, crotonaldehyde acrolein, benzaldehyde, furfural, and others.

The amine-aldehyde condensation products contain methylol or similar alkylol groups, and in most instances at least a portion of these alkylol groups are etherified by a reaction with an alcohol to provide

organic solvent-soluble resins. Any monohydric alcohol can be employed for this purpose, including such alcohols as methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol and others, as well as benzyl alcohol and other aromatic alcohols, cyclic alcohols, for example, cyclohexanol, monoethers or glycols such as Cellosolves and Carbitols™ (Union Carbide), and halogen-substituted or other substituted alcohols, such as 3-chloropropanol. The preferred amine-aldehyde resins are etherified with methanol or butanol.

A grind resin also may be used in the basecoat compositions of the present invention. While the grind resin may be comprised of a number of water soluble polyurethane resins, it is preferred that the grind resin be similar in chemical character to the principal or major vehicle resin, i.e., contain a polyester resin component comprised of a carboxylic acid component comprised of at least about 50% by weight of a C18 to C60 carboxylic acid, preferably a dicarboxylic acid. The grind resin may range between 2 and 75% by weight of the total solids in the coating composition and will vary depending on the desired color and preferably contains 5-40% by weight of the basecoat composition.

A preferred anionic polyurethane resin for use as a grind resin in embodiments of this invention is produced from a polyester polyol synthesized from dimer fatty acid, adipic acid, and 1,6-hexane diol. The resulting polyester diol is reacted with isophorone diisocyanate, dimethylol propionic acid and neopentyl glycol to produce a polyurethane intermediate which is capped with diethanolamine.

Pigments may be incorporated into the basecoat to provide the desired cosmetic characteristics. This is done by mixing pigments with the above-described grind resin and optionally, with other additives to form a pigment paste. Any standard pigment known in the art may be used with resins of the present invention so long as these pigments can be formulated without affecting the desired low flash and quick-drying characteristics.

Specific examples of the dye stuffs or pigments may be inorganic or organic, for example, graphite, carbon black, zinc chromate, strontium chromate, barium chromate, lead chromate, lead cyanide, titanium dioxide, zinc oxide, cadmium sulfide, iron oxide, aluminum flakes mica flakes, zinc sulfide, phthalocyanine complexes, naphthol red, quinacridones and halogenated thioindigo pigments, among others.

The preferred metallic pigments are metal powders preferably aluminum metal flakes. Preferred aluminum flake pigments are available from Silberline Corp, Lansford, Pennsylvania or from Eckart Werke, Guenterstahl, West Germany. The aluminum flake pigments provide the coating with an enhanced "metallic veneer". In a preferred embodiment of the present invention standard grade aluminum stabilized with phosphate ester is used. Other metallic flake pigments, for example, silver may also be used but these are usually prohibitive in cost and inferior in appearance. The metallic pigments may also be mixed with non-metallic pigments, but these are to be carefully chosen so as not to diminish the desired metallic effect.

The resins used in the basecoat are dispersed in deionized water. It is preferred that the deionized water have conductance readings of less than 13 microohms⁻¹ and most preferably less than about 5 microohms⁻¹ to prevent gassing caused by the reaction of aluminum with water. Deionized water is also chosen to avoid salts that naturally occur in tap water. Other solvents may also be employed with the deionized water. An especially preferred solvent is Butyl Cellosolve™ which aids mixing, formulating and dispersing pigment in the basecoat composition. Other solvents can also be used, for example, low-boiling mono and polyhydric alcohols, ethers, esters, ketones and other organics.

The organic solvent, which comprises at most about 80% of the basecoat composition, and preferably comprises about 10% to 20% by weight of the basecoat composition (including water) may be selected to promote the dispersibility of individual components in the final basecoat composition (plasticizer characteristics) and for its low volatility characteristics.

A rheology control agent is also preferably incorporated into the basecoat composition. The rheology control agent controls the viscosity of the resulting composition and is incorporated in amounts that will prevent sagging or running after a basecoat is sprayed onto a vertical surface such as an automobile body. The direct result of incorporating a rheology control agent is to provide flow control, body and sprayability. Other favorable results of adding a rheology control agent are to enhance the flip effect of metallic flake pigments, to deposit a thicker coating and to achieve complete coverage of a substrate. The sprayed coatings containing these agents also exhibit greater orientation of the metallic flake pigments on the final coated substrate. Rheology control agents which can be used in embodiments of the present invention include the fumed silica compounds and the bentonite clays. Preferred fumed silica compounds are the hydrophobic silica compounds, for example Aerosil™ R972, available from DeGussa Corporation, (Frankfurt, West Germany). Another rheology control agent which may be used, and in certain basecoat compositions, may be preferred is a synthetic sodium lithium magnesium silicate hectorite clay. An example of one such clay is Laponite™ RD, available from Laporte, Inc (Saddlebrook, New Jersey). In certain preferred embodiments rheology control agents are mixed. The rheology control agent when it is included, generally comprises about 0.1 to about 20 percent by weight of the basecoat composition and

preferably comprises between about 1 % and about 5 % by weight of the final basecoat composition.

In general, the particle size of the rheology control agent plays a role in the overall thixotropic properties of these resins. Rheology control agents in embodiments of this invention are suspended in the material. It may be proposed that the rheology control agents are suspended and function, at least in part, through coulombic or electrostatic interactions.

In general, the particle sizes can be from less than 0.1 μm to over about 200 μm . These sizes can be adapted to develop in part the rheology properties sought. In appropriate circumstances, the particle sizes may be from about 0.01 to about 10 μm .

In addition to a principal resin or major vehicle resin and a grind resin, preferred basecoat compositions also are comprised of at least about 5 % by weight of the resinous vehicle of a branched-chain polyester resin. The branched-chain polyester is added for improved application properties and improved physical properties (due to increased cross-link density). In general, the branched-chain polyester is produced from the same components as the polyester component except that in addition to the long and short chain carboxylic acid components, a small percentage of trifunctional acid or acid anhydride is used. Thus, the carboxylic acid component of the branch-chain polyester is comprised of at least 50 % by weight of at least one long-chain carboxylic acid having between 18 and 60 carbon atoms such as a long chain fatty acid, preferably C_{36} dimer fatty acid and no more than 50 % by weight, preferably no more than 48 % by weight of at least one short chain dicarboxylic acid such as isophthalic acid and a small percentage, preferably between 2 and 25 % by weight of a polyfunctional carboxylic acid or acid anhydride having at least 3 carboxylic acid groups such as trimellitic anhydride. In preferred embodiments, the branched chain polyester is synthesized from dimer fatty acid, isophthalic acid, and 1,6-hexane diol. A small percentage, between 2 and 25% of trimellitic anhydride is added to the polyesterification reaction to branch the polyester. The branched chain polyester is cooked to a final acid number of 10-50, and preferably, 20-40. In general, the branched polyester comprises about 20% of the resinous vehicle, but may be lower depending on the color.

Any additional agent used, for example, surfactants, fillers, stabilizers, wetting agents, dispersing agents, adhesion promoters, etc. may be incorporated into the basecoat composition. While the agents are well-known in the prior art, the amount used must be carefully controlled to avoid adversely affecting the coating and quick-drying characteristics.

In formulating the basecoat compositions of the present invention, the order of addition of the individual components is often very important. As a rule, the cross-linking agent in a solvent is added to the rheology control agent in solution and thoroughly mixed. Thereafter, the major vehicle resin dispersion (neutralized with amine) is added to the rheology control solution under agitation. If desired a slurry of aluminum metal flakes and/or mica particles (mica particles are used alone in the case where an aluminum metallic veneer is not desired) in Butyl Cellosolve™ is mixed with a premixed slurry of a branched-chain polyester resin and dimethylethanolamine. This mixture of aluminum is then agitated with the slurry containing resinous vehicle, cross-linking agent, and rheology control agent. Pigment pastes comprised of polyurethane resin, pigment, fillers, stabilizers, plasticizers and other additives may then be mixed under agitation with the above-resulting mixture. Pigment paste particles are prepared in a sand mill, attritor or other common milling equipment prior to use.

The pigment pastes may be prepared by mixing the aminoplast resin with about 1/4 of the total polyurethane resin to be added to the pigment paste. Pigment is added to this slurry under agitation for about 1/2 hour. The rest of the polyurethane resin is then added and the resulting paste is mixed for another half-hour. The pH and viscosity of the paste is checked and any adjustments are made by adding deionized water and/or tertiary amine. The weight ratio of pigment to binder usually ranges between 0.15-5.0. The amount of pigment ranges between 6 and 60% of the total weight of pigment plus binder. Other well-known methods of formulating prepared prepaint pastes may also be used.

The final basecoat composition is adjusted to a pH of 7.6-7.8 with a tertiary amine, for example, N-ethylmorpholine. Viscosity may be adjusted using deionized water. Final basecoat compositions preferably are comprised of the following components in the indicated weight ratios.

Table I

Ingredient	Amount (% by weight of Solids of Final Basecoat composition)
Polyurethane resin	20-80%
Melamine	5-50%
Rheology Control Agent	0-20%
Branched chain Polyester	0-35%
Pigment	2-65%

The basecoat compositions described hereinabove can be applied to a metal or plastic substrate in one or two coats using for example an air atomizer (Binks Model 60 spray gun, available from Binks Manufacturing Corporation, Franklin Park, Illinois), or by using other conventional spraying means. The basecoat compositions may also be applied electrostatically. The basecoat compositions are preferably sprayed at 3,4-5,5 bar, and a relative humidity of between 50 and 90% (optimally at 60-80% relative humidity) and a temperature of 21,1-32,2 °C.

After being deposited, the basecoat compositions in general are flash dried within a temperature range of about room temperature to about 62,8 °C for between 30 seconds and about 10 minutes using warm air blowing at a relative humidity of 5-40%. The preferred flash temperature is about 48,9 °C which is carried out for preferably between about 1 and 5 minutes. The flash conditions described herein result in about 90-95% of the solvents (water plus organics) being flashed from the basecoat in this short period of time.

After the first basecoat is deposited, a second basecoat can be deposited over the first without drying (flash off), or alternatively, a clearcoat may be deposited over the flashed basecoat. Any number of clearcoat compositions known in the art may be used. Any known unpigmented or other transparently pigmented coating agent is in principle, suitable for use as a clearcoat. A typical top coat composition contains 30-70% film forming resin and 30-70% volatile organic solvent.

After the clear coat is coated onto the basecoat layer, the multi-layer coating is then baked to cross-link the polymeric vehicle and to drive the small amount of residual water and organic solvent from the multi-layered polymeric composition. A preferred baking step involves heating the coated substrate for a period of 10-60 minutes at a temperature of between 65,6 and 148,9 °C. The baking step cures the coating to a hard, durable film.

The invention will be further described in connection with several examples which follow. These examples are shown by way of illustration of the invention and are not meant to limit the scope of the invention. All parts and percentages in the examples are by weight unless otherwise indicated.

Polyurethane Example 1

Preparation of a Polyurethane Resin

A polyester polyol resin is prepared by charging a reaction vessel (flask with a fractionating column) with 551.9 g (15.8 % of a polyester resin) of isophthalic acid, 1923 g. (54.9 %) Empol™ 1010 (dimer fatty acid available from Emery Chemical Co.), and 1025.1 g. (29.3 %) of 1,6-hexanediol and 100 g of toluene. Additional toluene may be added to fill the trap. The mixture was heated under nitrogen and the water of condensation was removed. During this heating 235.7 g of water was distilled off. Heating was continued at approximately 200 °C until the acid number is less than or equal to 8. The remaining toluene is then vacuum stripped at 200 °C to produce a polyester resin for use in the polyurethane resin.

At this point, 697.9 g of the above-synthesized polyester resin 43.0 g of dimethylol propionic acid, 16.1 g of neopentylglycol, 243.0 g of isophorone diisocyanate and 300 g of methyl isobutyl ketone are charged to the reactor and heated at reflux (about 128 °C) until a constant isocyanate value is obtained. 36.8 g of trimethylol propane is then added to the reactor and the batch is allowed to reflux for an additional one hour. At this point, the nitrogen purge is turned off and the batch is cooled to 95 °C. 28.6 g of dimethylethanolamine and 100 lbs (45500 g) of water is then added using a portion of the water as a rinse. The batch is then allowed to sit until it becomes homogeneous (about 5 minutes) and then 2048.71 g. of water is added over a 20 minute period under vigorous agitation.

At the end of this addition the mixture is distilled on high heat with vigorous agitation to remove water and methyl isobutyl ketone. The water is then returned to the batch and the approximately 300 grams of methyl isobutyl ketone which was distilled off is discarded. 238 g. of n-butanol is added and the batch is

held at 80 degrees C for 30 minutes. The batch is then dropped and filtered through a 10 micron filter to give a polyester-urethane vehicle for use in the basecoat composition of the invention. The resulting dispersion has a solids content of 30% and a Gardner viscosity of Z2.

5 Polyurethane Dispersion 2

Preparation of Polyester Resin

10 A reaction vessel is charged with 1995 g. of adipic acid, 1995 g. of dimer acid, and 2450 g. of 1,6-hexanediol, and 136 g. toluene. The mixture is heated under nitrogen to 209 degrees C, removing water until an acid number less than 8 is reached. Remaining toluene is vacuum stripped to produce a polyester resin having solids content greater than 98%.

Polyurethane Dispersion Preparation

15 857.4 g. of the above polyester is mixed with 14.6 g. neopentyl glycol, 53.1 g. dimethylolpropionic acid, 306.5 g. isophorone diisocyanate, 97.1 g. methyl ethyl ketone, and 235.0 g. methyl amyl ketone are refluxed until a constant isocyanate value is obtained. At this point, 24.8 g. of diethanolamine is added and the mixture is held for 30 minutes. 24.8 g. of dimethylethanolamine and 116.8 g. deionized water and 118.2
20 g. isopropyl alcohol are added and allowed to mix for 15 minutes. 3123.2 g. deionized water is then added over a 20 minute period with vigorous agitation. The resulting dispersion has a solids content of 26% and an appropriate Gardner viscosity.

Polyurethane Dispersion 3

25 Preparation of Polyester

770 g. dimer acid, 230 g. 1,6-hexanediol, and 25 g. toluene are charged and the resulting mixture heated to 200 degrees C. Heating is continued, removing water, until an acid number less than 10 is
30 achieved. The remaining toluene is then removed under vacuum.

Polyurethane

700 g. polyester above, 12.6 g. neopentyl glycol, 43 g. dimethylolpropionic acid, 244 g. isophorone diisocyanate, 77.8 g. methyl ethyl ketone, and 195.3 methyl amyl ketone are reacted using the procedure for polyurethane dispersion 2. The resulting dispersion has a solids content of 26% and a Gardner viscosity
35 of Z1.

Branched Polyester 1

40 2594 g. of dimer acid, 2564 g. of 1,6-hexanediol, and 744 g. of isophthalic acid are charged and the mixture heated to 195 degrees C under nitrogen with agitation until acid number of 10 or less is reached. The mixture is then cooled to 150 degrees C and 1000 g. of trimellitic anhydride is added slowly, and refluxed until an acid number of 30-32 is reached. After cooling to 150 degrees C or less, 729 g. of butyl
45 Cellosolve™ and 1459 g. of n-butanol are added. The resulting polyester has a solids content of 70% and a Gardner viscosity of U-V.

Branched Polyester 2

50 1230 g. dimer acid and 769.5 g. 1,6 hexanediol, are charged and heated to 195 degrees C under nitrogen with agitation. Heating is continued until an acid number less than 10 is reached. The mixture is then cooled to 150 degrees C and 420.1 g. trimellitic anhydride is added slowly and heated until the acid number falls below 30. 335 g. butyl glycol and 670 g. n-butanol are then added with agitation. The resulting polyester solution has a solids content of 70% and a Gardner viscosity of Z1.

55

Branched Polyester 3

868.7 g. 1,6 hexanediol, 1346.2 g. dimer acid, and 386 g. isophthalic acid are heated at 195 degrees C until an acid number less than 8 is achieved. 206.6 g. trimellitic anhydride is then added slowly under agitation and heat applied until an acid number less than 30 is achieved. A 2:1 mixture of n-butanol and butyl glycol are then added, until 70% solids is reached. The resulting branched polyester resin had a Gardner viscosity of U.

PREPARATION OF BASECOAT COMPOSITIONS

The composition of the basecoats is shown in Table 2, where the numbers denote parts by weight. The following notes refer to components listed there:

Thickener 1: Paste of Aerosil™ R972 (Degussa) hydrophobic fumed silica sand milled with appropriate polyurethane grind resin and melamine in water, organic solvent mixture at 11% strength.

Thickener 2: Paste of synthetic sodium lithium magnesium silicate hectorite clay, Laponite™ RD (Laporte), 2% strength in deionized water; the paste is prepared by stirring with Cowles blade in water for one hour.

Thickener 3: Paste of Laponite™ RD 3% strength in deionized water. Prepare as Thickener 2.

Titanium Dioxide Pigment Paste: 41% concentration of DuPont R-960 titanium dioxide sandmilled with appropriate polyurethane grind resin and melamine.

Melamine Resin: Commercially available methanol-etherfied melamine/formaldehyde resin, solids content 90% by weight in n-butanol.

Aluminum Pigment I: Silberline SS-5251 AR post treated with 4.5% Vircopet™ 40 (phosphate ester commercially available from Albright & Wilson, Richmond, Va.)

Aluminum Pigment II: Stapa Hydrolac™ WH-R607 from Eckart Werke

Aluminum Pigment III: Stapa Hydrolac™ WH-8487 from Eckart Werke

	1	2	3	4	5	6	7	8	9
Thickener 2	40	37		37	38				
Thickener 3			25					13	13
Melamine Resin	4	4	4	4	8	7	4	1	2
Butyl Cellosolve	1	1	1	1	1	2			1
Polyurethane 1 (30%NV)	40			40					18
Polyurethane 2 (26%NV)		44			42		38	17	
Polyurethane 3 (26%NV)			44			38			
Aluminum I (54%NV)	6			6		6	6		
Aluminum II (65%NV)		5							
Aluminum III (65%NV)			5		6				
Butyl Cellosolve	1	1	1		4	2	1		
Polyester 1 (70%)	6						6	3	
Polyester 2 (70%)			6	6					
Polyester 3 (70%)		6							
Dimethylethanolamine 5% Strength in Water	2	2	2	2	1	6	6	1	
Thickener 1						27	27	17	17
Titanium Dioxide Paste								48	49
Deionized Water			12	4		12	12		

EXAMPLES 1 to 4

The melamine resin and Butyl Cellosolve™ are premixed and added to the thickener under agitation. The polyurethane dispersion is then added to this mixture under agitation. An aluminum slurry is made by first mixing the aluminum pigment and butyl cellosolve, then adding the polyester resin, and then finally preneutralizing this slurry with the 5% DMEA solution. The aluminum slurry is then added to the polyurethane/thickener/melamine mixture under agitation.

Example 5

Half of the melamine resin and Butyl Cellosolve™ are premixed and added to the thickener under agitation. The polyurethane dispersion is then added. An aluminum slurry is made separately by mixing the aluminum pigment, remaining butyl Cellosolve™ and melamine resin. The aluminum slurry is then added under agitation to the rest of the paint. The pH is then adjusted with 5% dimethylethanolamine in water.

Example 6

An aluminum slurry is made with aluminum pigment, melamine resin, and Butyl Cellosolve under agitation. The polyurethane dispersion is added to the aluminum slurry. Thickener is then added under agitation. pH is adjusted with 5% DMEA and viscosity is adjusted with deionized water.

Example 7

The polyurethane dispersion, melamine resin, and Butyl Cellosolve™ are mixed with agitation. An aluminum slurry is made as in Example 1 to 5 and added to the first mixture under agitation. The thickener is added under agitation. Viscosity is adjusted with deionized water.

Examples 8 and 9

Melamine resin and Butyl Cellosolve are premixed and added under agitation to Thickener 3. The polyurethane dispersion is then added under agitation. In Example 8, the polyester resin is preneutralized with 5% DMEA and then added under agitation. Thickener 1 (R972 paste) is added and then the titanium dioxide paste is added both under agitation.

Claims

1. The use of an anionic polyurethane resin for producing waterborne basecoat compositions for multi-layer coatings prepared by
 - A) applying to the substrate a first layer of the waterborne basecoat composition
 - B) flash drying said first layer
 - C) applying at least one layer of a clear topcoat onto said basecoat and
 - D) curing said basecoat and topcoat to a hard, durable film,
 wherein said polyurethane resin has an acid number of at least about 10 and is obtained by at least partially neutralizing with base the free carboxylic acid groups of the reaction product of
 - a) a polyester polyol
 - b) a multi-functional compound having at least one active hydrogen functionality and at least one carboxylic acid functionality
 - c) optionally a compound having at least two active hydrogen groups but having no carboxylic acid groups and
 - d) a polyisocyanate,
 characterized in that said polyester polyol (a) is synthesized from a carboxylic acid component and an excess of a polyol component wherein said carboxylic acid component comprises at least 50 % by weight of at least one long-chain carboxylic acid having between 18 and 60 carbon atoms.
2. The use according to claim 1 wherein said carboxylic acid component comprises between 50 and 80 % by weight of at least one long-chain carboxylic acid having between 18 and 60 carbon atoms.
3. The use according to claim 1 or 2 wherein said long-chain carboxylic acid is C₃₆ dimer fatty acid.
4. The use according to claims 1 to 3 wherein said polyisocyanate (d) is an aliphatic diisocyanate or a mixture of aliphatic diisocyanates.
5. The use according to claims 1 to 4 wherein said multi-functional component (b) is 2,2-di-(hydroxymethyl)propionic acid.
6. A method of coating a substrate with a multi-layer coating comprising

- (A) applying to the substrate a first layer of waterborne basecoat composition comprising
 (i) an anionic polyurethane resin according to claim 1
 (ii) a pigment or a mixture of pigments
 (iii) a rheology control agent and
 (iv) a crosslinking agent
 (B) flash drying said first layer
 (C) applying at least one layer of a clear topcoat onto said basecoat and
 (D) curing said basecoat and topcoat to a hard, durable film.
7. The method according to claim 6 wherein said substrate is an automobile.
8. The method according to claim 6 or 7 wherein said carboxylic acid component comprises between 50 and 80 % by weight of at least one long-chain carboxylic acid having between 18 and 60 carbon atoms.
9. The method according to claims 6 to 8 wherein said long-chain carboxylic acid is C₃₆ dimer fatty acid.
10. The method according to claims 6 to 9 wherein said polyisocyanate (d) is an aliphatic diisocyanate or a mixture of aliphatic diisocyanates.
11. The method according to claims 6 to 10 wherein said multifunctional compound (b) is 2,2-di-(hydroxymethyl)propionic acid.
12. The method according to claims 6 to 11 wherein said pigment is an aluminium flake pigment.
13. The method according to claims 6 to 12 wherein said crosslinking agent comprises an aminoplast resin.
14. The method according to claims 6 to 13 wherein said waterborne basecoat composition further comprises a branched chain polyester resin which is synthesized from a carboxylic acid component and a polyol component wherein said carboxylic acid component comprises at least 50 % by weight of at least one long-chain carboxylic acid having between 18 and 60 carbon atoms, no more than 48 % by weight of at least one short-chain dicarboxylic acid and between 2 and 25 % by weight of a polyfunctional carboxylic acid or acid anhydride having at least 3 carboxylic acid groups.

Patentansprüche

1. Verwendung eines anionischen Polyurethanharzes zur Herstellung von Basislackzusammensetzungen auf Wasserbasis für Mehrschichtlacke, die dadurch hergestellt werden, daß man
 A) das Substrat mit einer ersten Schicht der Basislackzusammensetzung auf Wasserbasis versieht,
 B) diese erste Schicht unter Ablüften trocknet
 C) den Basislack mit mindestens einer Schicht aus einem Klardecklack überzieht und
 D) den Basislack und Decklack zu einem harten, dauerhaften Film aushärtet,
 wobei das Polyurethanharz eine Säurezahl von mindestens etwa 10 aufweist und durch zumindest teilweise Neutralisierung der freien Carbonsäuregruppen des Umsetzungsprodukts aus
 a) einem Polyesterpolyol,
 (b) einer polyfunktionellen Verbindung mit mindestens einer wasserstoffaktiven Funktionalität sowie mindestens einer Carbonsäurefunktionalität,
 (c) gegebenenfalls einer Verbindung mit mindestens zwei wasserstoffaktiven Gruppen, jedoch ohne Carbonsäuregruppen sowie
 (d) einem Polyisocyanat erhalten wird,
 dadurch gekennzeichnet, daß das Polyesterpolyol (a) aus einer Carbonsäurekomponente und einem Überschuß an Polyolkomponente synthetisiert wird, wobei die Carbonsäurekomponente zu mindestens 50 Gew.-% aus mindestens einer langkettigen Carbonsäure mit 18 bis 60 Kohlenstoffatomen besteht.
2. Verwendung nach Anspruch 1, bei der jene Carbonsäurekomponente zu 50 bis 80 Gew.-% aus mindestens einer langkettigen Carbonsäure mit 18 bis 60 Kohlenstoffatomen besteht.
3. Verwendung nach Anspruch 1 oder 2, bei der es sich bei der langkettigen Carbonsäure um C₃₆-Dimerfettsäure handelt.

4. Verwendung nach Ansprüchen 1 bis 3, bei der das Polyisocyanat (d) ein aliphatisches Diisocyanat oder eine Mischung aus aliphatischen Diisocyanaten darstellt.
5. Verwendung nach Ansprüchen 1 bis 4, bei der die polyfunktionelle Komponente (b) 2,2-Di-(hydroxymethyl)propionsäure darstellt.
6. Verfahren zur Beschichtung eines Substrats mit einem Mehrschichtlack, das darin besteht, daß man
(A) das Substrat mit einer ersten Schicht aus einer Basislackzusammensetzung auf Wasserbasis versieht, die aus
(i) einem anionischen Polyurethanharz nach Anspruch 1,
(ii) einem Pigment oder einer Mischung aus Pigmenten,
(iii) einem die Rheologie regulierenden Mittel sowie
(iv) einem Vernetzungsmittel besteht,
(B) diese erste Schicht unter Ablüften trocknet,
(C) den Basislack mit mindestens einer Schicht aus einem Klardecklack überzieht und
(D) den Basislack und Decklack zu einem harten, dauerhaften Film aushärtet.
7. Verfahren nach Anspruch 6, bei dem das Substrat ein Automobil darstellt.
8. Verfahren nach Anspruch 6 oder 7, bei dem die Carbonsäurekomponente zu 50 bis 80 Gew.-% aus mindestens einer langkettigen Carbonsäure mit 18 bis 60 Kohlenstoffatomen besteht.
9. Verfahren nach Ansprüchen 6 bis 8, bei dem die langkettige Carbonsäure C₃₅-Dimerfettsäure darstellt.
10. Verfahren nach Ansprüchen 6 bis 9, bei dem das Polyisocyanat (d) ein aliphatisches Diisocyanat oder eine Mischung aus aliphatischen Diisocyanaten darstellt.
11. Verfahren nach Ansprüchen 6 bis 10, bei dem die polyfunktionelle Verbindung (b) 2,2-Di-(hydroxymethyl)propionsäure darstellt.
12. Verfahren nach Ansprüchen 6 bis 11, bei dem das Pigment ein Aluminiumschuppenpigment darstellt.
13. Verfahren nach Ansprüchen 6 bis 12, bei dem das Vernetzungsmittel aus einem Aminharz besteht.
14. Verfahren nach Ansprüchen 6 bis 13, bei dem die Basislackzusammensetzung auf Wasserbasis weiterhin ein verzweigtkettiges Polyesterharz enthält, das aus einer Carbonsäurekomponente und einer Polyolkomponente synthetisiert wird, wobei die Carbonsäurekomponente zu mindestens 50 Gew.-% aus mindestens einer langkettigen Carbonsäure mit 18 bis 60 Kohlenstoffatomen, zu nicht mehr als 48 Gew.-% aus mindestens einer kurzkettigen Dicarbonsäure und zu 2 bis 25 Gew.-% aus einer polyfunktionellen Carbonsäure oder deren Anhydrid mit mindestens 3 Carbonsäuregruppen besteht.

Revendications

1. Utilisation d'une résine de polyuréthane anionique pour produire des compositions d'enduit de fond en suspension dans l'eau pour peintures multicouches préparée par
(A) l'application au support d'une première couche de la composition d'enduit de fond en suspension dans l'eau
(B) le séchage par évaporation de ladite première couche
(C) l'application d'au moins une couche d'un enduit de finition transparent sur ledit enduit de fond et
(D) la cuisson desdits enduit de fond et enduit de finition en une pellicule dure et résistante,
où ladite résine de polyuréthane a un indice d'acide d'au moins environ 10 et est obtenue en neutralisant au moins en partie avec une base les groupes "acide carboxylique" libres du produit de réaction de
(a) un polyol de polyester
(b) un composé multifonctionnel ayant au moins une fonctionnalité "hydrogène actif" et au moins une fonctionnalité "acide carboxylique"
(c) le cas échéant un composé ayant au moins deux groupes "hydrogène actif" mais n'ayant aucun groupe "acide carboxylique" et

- (d) un polyisocyanate,
caractérisée en ce que ledit polyol de polyester (a) est synthétisé à partir d'un composant "acide carboxylique" et d'un excès d'un composant "polyol", où ledit composant "acide carboxylique" comprend au moins 50 % en poids d'au moins un acide carboxylique à longue chaîne ayant entre 18 et 60 atomes de carbone.
2. Utilisation selon la revendication 1, où ledit composant "acide carboxylique" comprend entre 50 et 80% en poids d'au moins un acide carboxylique à longue chaîne ayant entre 18 et 60 atomes de carbone.
 3. Utilisation selon la revendication 1 ou 2, où ledit acide carboxylique à longue chaîne est un acide gras dimère en C₃₆.
 4. Utilisation selon les revendications 1 à 3, où ledit polyisocyanate (d) est un diisocyanate aliphatique ou un mélange de diisocyanates aliphatiques.
 5. Utilisation selon les revendications 1 à 4, où ledit composant multifonctionnel (b) est l'acide 2,2-di-(hydroxyméthyl)-propionique.
 6. Méthode pour peindre un support avec une peinture multicouche comprenant
 - (A) l'application au support d'une première couche de composition d'enduit de fond en suspension dans l'eau comprenant
 - (i) une résine de polyuréthane anionique selon la revendication 1
 - (ii) un pigment ou un mélange de pigments
 - (iii) un agent de contrôle rhéologique et
 - (iv) un agent de réticulation
 - (B) le séchage par évaporation de ladite première couche
 - (C) l'application d'au moins une couche d'un enduit de finition transparent sur ledit enduit de fond et
 - (D) la cuisson desdits enduit de fond et enduit de finition en une pellicule dure et résistante.
 7. Méthode selon la revendication 6, où ledit support est une automobile.
 8. Méthode selon la revendication 6 ou 7, où ledit composant "acide carboxylique" comprend entre 50 et 80% en poids d'au moins un acide carboxylique à longue chaîne ayant entre 18 et 60 atomes de carbone.
 9. Méthode selon les revendications 6 à 8, où ledit acide carboxylique à longue chaîne est un acide gras dimère en C₃₆.
 10. Méthode selon les revendications 6 à 9, où ledit polyisocyanate (d) est un diisocyanate aliphatique ou un mélange de diisocyanates aliphatiques.
 11. Méthode selon les revendications 6 à 10, où ledit composant multifonctionnel (b) est l'acide 2,2-di-(hydroxyméthyl)-propionique.
 12. Méthode selon les revendications 6 à 11, où ledit pigment est un pigment pailleté d'aluminium.
 13. Méthode selon les revendications 6 à 12, où ledit agent de réticulation comprend une résine aminoplaste.
 14. Méthode selon les revendications 6 à 13, où ladite composition d'enduit de fond en suspension dans l'eau comprend en outre une résine de polyester ramifiée qui est synthétisée à partir d'un composant "acide carboxylique" et d'un composant "polyol", dans laquelle ledit composant "acide carboxylique" comprend au moins 50% en poids d'au moins un acide carboxylique à longue chaîne ayant entre 18 et 60 atomes de carbone, pas plus de 48% en poids d'au moins un acide dicarboxylique à chaîne courte et entre 2 et 25% en poids d'un acide carboxylique multifonctionnel ou un anhydride d'acide ayant au moins 3 groupes "acide carboxylique".